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XLVIII. — *THE VISCOSITY OF MERCURY VAPOR.*

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THE VISCOSITY OF MERCURY VAPOR.

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The uncertainty which attaches to the specific heat ratio of gases as a means of distinguishing between monatomic and polyatomic molecules has been recently made evident by the extended discussions of the significance of that property in connection with the atomic weights of argon and helium. It is therefore of great interest to investigate other properties which may be expected to be related to the atomicity of the molecule. Of such properties those dependent on the volume or cross-section of the molecules seem most promising. We have therefore undertaken the investigation of one of these, the viscosity or internal friction, in order to determine whether a marked difference in its value exists in the case of gases with monatomic and those with polyatomic molecules. To this end we have made comparative measurements of the viscosity of hydrogen, carbon dioxide, and mercury vapor at the boiling temperature of the last named substance.

According to the Kinetic Theory of Gases the viscosity coefficient has the theoretical significance expressed by the following equation,*

$$\eta = \frac{1}{\pi} NmLc,$$

in which N is the number of molecules in the unit of volume, m the mass of a single molecule, L the mean free path, and c the mean velocity. Moreover, the free path L is dependent solely on the number of molecules N and the mean cross-section q of a single molecule, or its sphere of action.†

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* O. E. Meyer, Kinetische Theorie der Gase, 1st ed., pp. 130, 139.

† Ibid., pp. 206, 218. The symbol Q used by the author represents the total cross-section of all molecules in the unit of volume, and is therefore evidently equal to Nq.

$$L = \frac{1}{4\sqrt{2}\,Nq},$$

whence it follows that

$$\eta = \frac{1}{4\pi\sqrt{2}}\,\frac{mc}{q};$$

or for any two different gases,

$$\eta_1 : \eta_2 = \frac{m_1 c_1}{q_1} : \frac{m_2 c_2}{q_2}.$$

But, since for any two gases at constant temperature,

$$m_1 {c_1}^2 = m_2 {c_2}^2,$$

the above proportion may be simplified to the following equation:

$$\frac{q_1}{q_2} = \frac{\eta_2}{\eta_1}\,\sqrt{\frac{m_1}{m_2}}; \qquad (1)$$

from which it is evident that the relative mean cross-sections of the molecules of the two gases are readily calculated from their molecular weights and viscosity coefficients. It was thought by us that monatomic molecules might prove to be much smaller than polyatomic ones, since it seems *a priori* not improbable that the spaces between the atoms of the latter are large in comparison with the dimensions of the atoms themselves. The experiments to be here described show, however, that no marked distinction exists between monatomic and polyatomic gases in this respect.

Experiments on the viscosity of mercury vapor, and especially on the effect of temperature upon it, have been already made by S. Koch,* who calculated that at 300° the volume of mercury molecule is 4.4 as great as that of the hydrogen molecule. As this calculation was not based on direct comparative experiments made by passing the two gases through the same capillary, but was an indirect one involving the measurements of different experimenters, and the dimensions of the capillaries used by them, it seemed desirable to subject the matter to further investigation in the direct manner indicated. Moreover, the author does not discuss the significance of his result in its bearing on the relative magnitude of atoms and molecules.

The method used by us in determining the relative viscosity consisted

* Wied. Ann. Phys. Chem., XIX. 857, 1883.

in measuring the quantities of the different gases which under a constant difference of pressure passed in a given time through the same capillary kept at a definite constant temperature. O. E. Meyer * has derived the following formula for calculating the viscosity coefficient of a gas from its rate of flow through a capillary tube:

$$\eta = \frac{\pi}{16} \frac{R^4}{\lambda} \frac{(p_1^2 - p_2^2)\, t}{p_1 V_1},$$

where λ is the length and R the radius of the tube, t the time, p_1 the pressure at which the gas enters and p_2 at which it leaves the tube, and V_1 the volume of the transpired gas measured at the pressure p_1. In case of comparative experiments made with the same capillary on two different gases, the following proportion holds true:

$$\eta_1 : \eta_2 :: \frac{(p_1^2 - p_2^2)_1\, t_1}{n_1} : \frac{(p_2^2 - p_2^2)_2\, t_2}{n_2}, \qquad (2)$$

in which n_1, n_2, represent respectively the number of gram molecular weights of the two gases transpired, — since n is proportional to the product pV.

The apparatus and experimental method that we employed were necessarily quite different from the usual ones, and they will therefore be briefly described. The capillary used in the most complete series of experiments consisted of a glass tube about 74 cm. in length and 0.34 mm. in internal diameter (determined by measuring the volume of a known length by means of mercury). A smaller capillary about 49 cm. in length and 0.22 mm. in diameter was used in a preliminary series. The capillary was bent in the manner shown in Figure 1, except that, as actually constructed, it was made much more compact. To its ends were fused pieces of ordinary glass tube, as shown in the figure; one of these was provided at the point A with a ground glass joint. The capillary was placed in a vertical position in a heavy steel cylinder (see A, Fig. 2) 30 cm. high, 2.8 cm. internal diameter, having a small orifice at the side, through which the ground joint protruded for a distance of about one centimeter. The capillary was held in position in the orifice by packing with loose asbestos. Although the capillary was vertical, the influence of gravity was eliminated by reason of the fact that the ascending and descending parts were made equal in length. The top of the cylinder was closed by an iron plate screwed down with a nut, N; the nut and

* Pogg. Ann., CXXVII. 269.

the plate were perforated in the centre, and into the latter was welded an open iron tube *B*, projecting 25 cm. in length and 1½ cm. in diameter. The cylinder was covered, except on the bottom, with a jacket of asbestos about 5 cm. thick, and the projecting tube *B*, which was to serve as a condenser, was wound with spirals of copper wire to increase the cooling surface. Pure mercury was placed in the cylinder and boiled vigorously by means of a number of lamps beneath. The capillary was thus kept at the boiling temperature of mercury under atmospheric pressure. No regard was paid to the variations of temperature arising from changes in barometric pressure, as their effect would evidently be entirely negligible.

Any desired difference of pressure at the two ends of the capillary was attained by inserting a tube in the ground joint and connecting it with a large air reservoir, *R*, which was itself connected through the cock *S* with a suction pump and with an open mercury manometer, *M*. The gas or vapor entered at the other end of the capillary always under atmospheric pressure. The whole apparatus in the form used for measuring the rate of transpiration of the mercury vapor is shown in Figure 2.

In making the experiments, the rate of flow of the mercury vapor was first determined in the following manner. While the cylinder was being heated, carbon dioxide was forced through the capillary to prevent the condensation in it of liquid mercury and the formation of its oxide. After the mercury was boiling actively, and its vapor entirely enveloped the capillary, as shown by a mercurial thermometer inserted into the tube *B* (Fig. 2), it was connected with the suction pump, and mercury vapor drawn through for half an hour. The carefully ground end of a weighed bulb, *W*, was then inserted in the ground joint, its other end being connected by means of a clamped rubber tube, *C*, with the air reservoir, in which the desired reduction of pressure had been produced. At a definite moment the clamp *C* was opened and the time noted. As the volume of the condensing bulb *W* was very small compared with the volume of the air reservoir, no sensible change in the pressure was thus produced. The mercury vapor was found to be completely condensed in *W* about two to three centimeters from the ground joint. It was found that a slight and unavoidable leakage * through the ground joint occurred, and it was therefore necessary to readjust the pressure occasionally. It

* In the case of the mercury experiments no error could arise from this source, as the leakage was inward. In the case of those of carbon dioxide and hydrogen, it was proved by blank experiments that the amounts of carbon dioxide and water which leaked in were less than one per cent of the total weight.

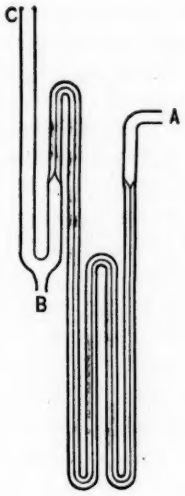

Fig. 1.

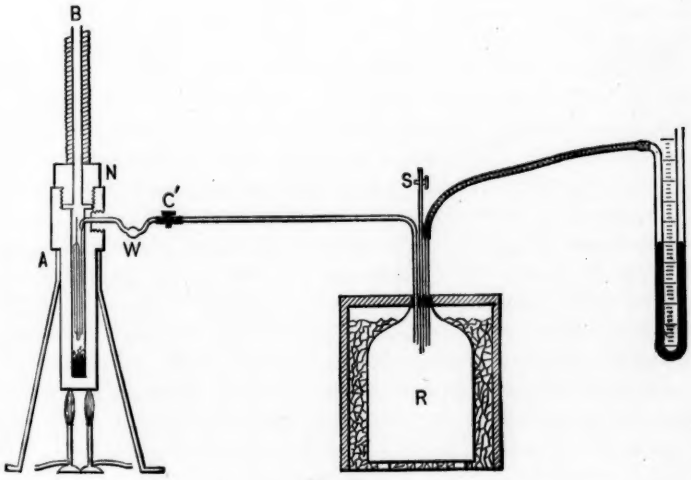

Fig. 2.

could easily be maintained constant to 0.2 or 0.3 mm., or even closer. After a sufficient time, usually sixty minutes, the clamp was closed, and at a noted instant the bulb was removed and subsequently weighed. Check experiments were made in this way at each of two or three different pressures.

The capillary was now removed from the cylinder and the opening B (Fig. 1) carefully closed by fusion. A glass tube long enough to project beyond the upper end of B (Fig. 2) was fused into the end C, and the capillary was then ready for the experiments with carbon dioxide and hydrogen. It was replaced in the cylinder as before, and the glass tube projecting through B connected through suitable wash-bottles with the gas generator. The carbon dioxide was made in a Kipp generator by the action of dilute sulphuric acid on lumps of pure fused sodium carbonate, and was dried by passing through two Allihn gas wash-bottles containing strong sulphuric acid. The hydrogen was prepared from pure Bertha zinc and dilute sulphuric acid, was washed with caustic soda solution and dried by sulphuric acid, as in the case of the carbon dioxide. In order to maintain the gas entering the capillary at atmospheric pressure, a T-tube was inserted between the wash-bottles and the capillary, and its perpendicular arm was turned downwards and caused to dip into sulphuric acid barely below its surface. The cock of the generator was opened sufficiently to cause the gas to bubble out steadily through the sulphuric acid.

The transpiration measurements were made as in the case of mercury. The carbon dioxide flowing through in a definite time was determined by absorption in weighed tubes filled with lumps of soda lime. The hydrogen was burnt by passing it over hot copper oxide contained in hard glass tubes from which the air was previously displaced by carbon dioxide, and the water collected in weighed calcium chloride tubes.

The results are presented in the following table. In the first column is given the symbol of the substance; in the second, the atmospheric pressure p_1; in the third, the difference in pressure $(p_1 - p_2)$; in the fourth, the time t expressed in hours; in the fifth, the weight w in grams of the substance weighed; in the sixth, the mean weight transpired in one hour as computed from the separate check experiments; and in the last, the quotient obtained by dividing this weight by the molecular weight m of the substance, the time, and the pressure function $(p_1^2 - p_2^2)$.*

* In the calculation of this quantity the same mean value of p_1 was used in all the experiments of each series, namely, 760 for those with the smaller capillary, 765 for those with the larger.

(See expression (2), page 229.) As the headings indicate, the first of these two series of experiments was made with the smaller, and the second with the larger capillary. It will be seen that in the second series two sets of determinations are given for mercury vapor: the first of these was made before and the second one after the experiments with carbon dioxide and hydrogen, and their agreement shows that the capillary had undergone no change by stoppage or otherwise during the course of the experiments with it.

SERIES I.

Small Capillary.

	p_1	$p_1 - p_2$	t	w	$w : t$	$\frac{w \times 10^{10}}{tm(p_1^2 - p_2^2)}$
Hg	753	200	1½	0.738		
	753		1½	0.740		
	756		1½	0.745	0.494	93.6
	755	300	1	0.685		
	755		1	0.686	0.686	93.6
	754	400	1	0.834		
	754		1	0.831	0.833	93.9
CO_2	752	200	1	0.237		
	752		1	0.239		
	752		1½	0.357	0.238	205
	759	300	1	0.329		
	759		1	0.327		
	766		1	0.324	0.327	203
	766	400	1	0.400		
	766		1	0.396		
	759		1	0.396	0.397	202

Attention may be first called to the agreement of the values of the last column in the case of the transpiration of the same substance under different differences of pressure, thus proving that the effect of pressure is in close accordance with that required by the formula, and consequently that the capillaries are of sufficient length and small enough bore to give the true values of the viscosity coefficients.

Of the two series of experiments the first one made with the smaller capillary is to be regarded as the less reliable by reason of the fact that, owing to an accident to the capillary, check experiments with mercury

SERIES II.

LARGE CAPILLARY.

	p_1	$p_1 - p_2$	t	w	$w : t$	$\frac{w \times 10^{10}}{tm(p_1^2 - p_2^2}$
Hg	769	150	1	1.548		
	769		1	1.548	1.548	374
	769	300	1	2.763		
	769		1	2.764		
	769		1	2.739	2.755	373
CO_2	765	150	1	0.704		
	765		1	0.706	0.705	774
	765	300	1	1.267		
	765		1	1.264	1.265	779
H_2	766	150	1	0.557		
	766		1	0.557	0.557	1517
	766	300	1	1.009		
	766		1	1.006	1.008	1496
Hg	766	300	1	2.728		
	766		1	2.746		
	764		1	2.743	2.739	371

vapor after completion of those with carbon dioxide could not be made as in the former case, in consequence of which it is not certain that a stoppage did not occur in the course of the series. While there was nothing to indicate that such was the case, yet on account of its extremely small bore it was much more liable to stoppage than the larger capillary. We consider the experiments with the latter to be certainly accurate within two per cent.

Nevertheless the agreement between the results of the first and second series is perhaps as close as could be expected with capillaries so different from each other in character. The relative viscosity coefficients of the different gases were calculated from the values of the last column in the table by means of formula (2). The results are as follows.

FIRST SERIES.

$$\frac{\eta_{Hg}}{\eta_{CO_2}} = 2.17.$$

SECOND SERIES.

$$\frac{\eta_{Hg}}{\eta_{CO_2}} = 0.08. \qquad \frac{\eta_{Hg}}{\eta_{H_2}} = 4.04. \qquad \frac{\eta_{CO_2}}{\eta_{H_2}} = 1.94.$$

The relative values for mercury and carbon dioxide agree within about four per cent. That of the second series is, however, more reliable, for the reason above stated, and will be used in the subsequent calculations. It may be stated that the value of the ratio $\eta_{CO_2} : \eta_{H_2}$ at ordinary temperature is 1.72,* somewhat smaller than that found by us at 357°, a result which is in accordance with the greater temperature coefficient of carbon dioxide established by several investigators.

The corresponding values of the relative mean cross-sections as calculated by formula (1) are

$$\frac{q_{Hg}}{q_{CO_2}} = 1.02; \quad \frac{q_{Hg}}{q_{H_2}} = 2.48.$$

That is to say, the average cross-section of the mercury molecule or atom is very nearly the same as that of the carbon dioxide molecule, and is about 2½ times as large as that of the hydrogen molecule. This last result does not differ very greatly from that (2.68) corresponding to the relative molecular volumes of mercury and hydrogen as calculated for 300° by Koch.

These results indicate that *atoms and molecules are of the same order of magnitude*, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves, and consequently the viscosity of gases, or any other property which like it is dependent only on the size or form of the molecules, is not adapted for distinguishing between monatomic and polyatomic molecules.

In considering the significance of the above values of the cross-section, the different masses of the various molecules, to be sure, ought not to be entirely disregarded. The mercury and carbon dioxide molecules have, as we have seen, the same cross-section, and therefore, assuming both to be of the same general form, they occupy the same volume. The mass of the former is, however, 4.55 times as great as that of the latter. The density of the mercury molecule is consequently greater in this same proportion. But this difference is not marked enough to make it neces-

* O. E. Meyer, Kinetische Theorie der Gase, p. 142.

sary to attribute it to free spaces within the carbon dioxide molecule. For it is not improbable that the inherent density of massive atoms like those of mercury may be considerably greater than that of light atoms, such as those of carbon and oxygen.

In closing, we desire to point out that the principle here established, that atoms and molecules are of the same order of magnitude, and that no considerable free interatomic spaces exist within the molecule, is in accordance with the remarkable fact that the molecular cross-section of most comparatively simple molecules is approximately an additive property calculable from certain constant values of the atomic cross-section.* This fact would be unintelligible, were the principle not correct; for if considerable space existed between the atoms, it is not to be supposed that those spaces would be the same in entirely dissimilar molecules, — that, for example, the space between the hydrogen and chlorine atoms in hydrochloric acid would have any relation to the space between the atoms in the elementary gases hydrogen and chlorine.

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* See O. E. Meyer, Kinetische Theorie der Gase, p. 209.

Rogers Laboratory of Physics,
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